Recycling the copper based spent catalyst for catalytic combustion of VOCs

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Abstract

The catalytic combustions of benzene, toluene and *o*-xylene (BTX) were investigated over the copper based spent catalyst and the pretreated copper based spent catalysts as well. Air, hydrogen and five different acid aqueous solution (HNO_3, CH_3COOH, H_2SO_4, HCl, and H_3PO_4) pretreatments were employed to recycle the spent catalyst from chemical industry. The properties of the pretreated spent catalysts were characterized by the Brunauer Emmett Teller (BET), elemental analyzer (EA), inductively coupled plasma (ICP), temperature programmed reduction (TPR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. The results showed that while the air pretreatment had an insignificant effect on the catalytic activity of the spent catalyst, the hydrogen pretreatment significantly enhanced that of the spent catalyst. The temperature of hydrogen pretreatment also made a significant difference in its catalytic activity. Furthermore, the increasing pretreatment temperature increased the catalytic activity of the spent catalyst, which was associated with the lower copper oxidation state (or reduced state). In acid pretreatment, the order of catalytic performance of the pretreated spent catalyst according to each acid aqueous solution was found to be HNO_3 > CH_3COOH > none > HCl > H_3PO_4 > H_2SO_4. Nitric acid or acetic acid pretreatment slightly improved the catalytic activity of the spent catalyst by regenerating the active sites on the pretreated samples. The XRD, XPS and TPR results clearly supported that all copper species such as CuO, Cu_2O and Cu^0 were active, among which Cu^0 was the most active for the removal of toluene. Hydrogen pretreatment was superior to air or acid pretreatments for regenerating the spent catalyst because it favored the generation of metallic coppers. Based on the results of a long-term test and the catalytic activity of BTX, we suggested that the copper based spent catalyst pretreated with hydrogen could be recycled for the removal of volatile organic compounds (VOCs).
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Keywords: Catalytic combustion; Spent catalyst; Pretreatment; Recycle; VOCs

1. Introduction

Volatile organic compounds (VOCs) are known as harmful pollutants because of their toxic, malodorous, mutagenic and carcinogenic nature, and their relatively high vapor pressure [1,2]. In addition, VOCs act indirectly as ozone precursors and smog precursors [3]. Therefore, proper control and reduction of VOCs emission from various industrial processes should be required to prevent and reduce the pollution of the atmosphere. In Korea, the Ministry of Environment recently proposed a stringent legislation that requires small-scale industries to install facilities to reduce even a small amount of VOCs emissions. Therefore, cost-effective and efficient technologies are needed for the removal of VOCs. There are several techniques for destruction of VOCs including thermal combustion and catalytic combustion. Although both thermal and catalytic combustions have been reported to be the most important technologies, the catalytic combustion is more efficient than thermal combustion owing to its low thermal NO_x emissions, low operating cost, and high destructive efficiency [4–6]. At present, catalysts such as noble metals (Pt, Pd) [7–11] and metal oxides [12–16] are extensively used in treating VOCs with different advantages and limitations.

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On the other hand, various commercial catalysts used in chemical-related applications have been disposed as industrial wastes when the activities of catalysts are insufficient to achieve the optimum yields. The main causes of catalytic deactivation are known to be fouling, poisoning and thermal degradation (or sintering). Fouling involves deposition of materials (e.g., coke deposition) on a catalyst surface to block the active sites. Poisoning involves strong chemical interaction of a component (e.g., sulfur) of the feed or products with active sites on the catalyst surface. Thermal degradation of catalyst decreases active sites because of agglomerations [17]. Deciding whether to regenerate or dispose the deactivated catalyst or to use it in other applications is closely connected to the chemical, economical, and environmental issues. Even though the activities and selectivities of the regenerated catalysts may not be good enough to reapply to the original process, it seems that they are good enough at least to be employed as catalysts for the catalytic combustion of VOCs because its reaction is non-selective (complete oxidation). If the catalyst for the removal process of VOCs can be replaced by the regenerated catalysts, it would be a highly preferable choice in eco-friendly catalyst based systems.

The spent catalysts containing noble and metal oxides seem to be still applicable for catalytic combustion if a proper regeneration method is applied. Developing a reliable regeneration method for spent catalyst is justifiable from the viewpoint of economic utilization and environmental protection. However, little attention has been given to the regeneration methods of the spent catalysts and the catalytic performance of regenerated catalysts. Therefore, systematic approaches are needed to assess the possibility of those materials to be applied in the catalyst-based processes for VOCs removal.

Kim [13] and Wang [18] have reported that copper based catalyst was the most active among the metals based catalysts for the combustion of aromatic hydrocarbons. In this work, the catalytic combustions of benzene, toluene or *o*-xylene (BTX) were examined over the copper based spent catalyst modified by pretreatment techniques to reuse the spent catalyst for the removal of VOCs. Air, hydrogen and five different acid (HCl, H_2SO_4, HNO_3, H_3PO_4 and CH_3COOH) pretreatment methods were employed. The best regeneration method was chosen by comparing the catalytic activities of the different pretreated spent catalysts.

2. Experimental

2.1. Catalysts

The copper based spent catalyst disposed off as an industrial waste was obtained from LG petrochemical company, Korea. Its basic properties are summarized in Table 1. To examine the influences of gas treatments for the spent catalysts, they were pretreated with 100 ml min^{-1} flow rate of air or hydrogen at three different temperatures (200, 300, and 400 °C) for 1 h, respectively. In addition, five different kinds of acid aqueous solutions (0.1N concentration: HNO_3, CH_3COOH, H_2SO_4, HCl, and H_3PO_4) were also used to pretreat the spent catalyst.

Table 1
The basic properties of the copper based spent catalyst

Catalyst	Cu/Al_2O_3
Shape	Sphere
Size (mm)	1.2
Color	Black
BET surface (m^2 g^{-1})	156
Cu concentration[a] (wt%)	7.9

[a] Copper concentration measured with ICP.

The acid treatments were performed in a 100 ml Erlenmeyer flask. In each experiment, a 2.0 g of the spent catalyst was put into the flask containing 50 ml of acid aqueous solution and then the mixture was stirred in a shaker (KMC-8480SF, Vision Scientific Co.) at a rate of 150 rpm at a room temperature for 5 h. The acid treated samples were washed further with deionized water until the pH of the solution reached 7 and dried at 120 °C for 24 h.

2.2. Characterization of catalysts

The Brunauer Emmett Teller (BET) surface areas of the spent catalyst and pretreated samples were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 analyzer. The crystal structures of samples used in this work were examined by X-ray diffraction (XRD) data using a Phillips PW3123 diffractometer equipped with a graphite monochromator and Cu Kα radiation of wavelength 0.154 nm. The samples used were investigated in the 2θ range of 20–90° at a scanning speed of 70°/h. The coke deposition and sulfur were measured by elemental analyzer (EA, 1110, CE Instruments). To determine the net amount of copper, inductively coupled plasma (ICP) was employed using a Perkin-Elmer OPTIMA 4300DV. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a photoelectron spectrometer VG Scientific MultiLab 2000 system equipped with a non-monochromatic Mg Kα radiation of 1253.6 eV. The C 1s peak (285.0 eV) was used for the calibration of binding energy values. The pressure in the analytical chamber was about 10^{-9} Pa. Temperature programmed reduction (TPR) was performed using ChemBET 3000 setup. The gas mixture (10% H_2 and 90% He) was passed through the catalyst sample (0.4 g) at a rate of 60 ml min^{-1}, while the temperature was increased up to 600 °C at a rate of 10 °C min^{-1}.

2.3. Catalytic combustion

The catalytic combustions were carried out using a conventional fixed bed flow reactor as shown in Fig. 1. The reactor has three major sections: (1) apparatus for preparation of vapors, (2) fixed bed flow reactor in a heating system, and (3) apparatus for the analysis of reactants and products. The catalytic reactor (quartz tube) was consisted of a vertical tubular with 1.2 cm diameter and 35 cm length in which the electrical heating system controlled by a proportional integral derivative (PID) controller. In order to get an accurate measurement of the catalyst temperature, K type thermocouple was positioned in the catalyst bed. A catalyst sample of 1.0 g
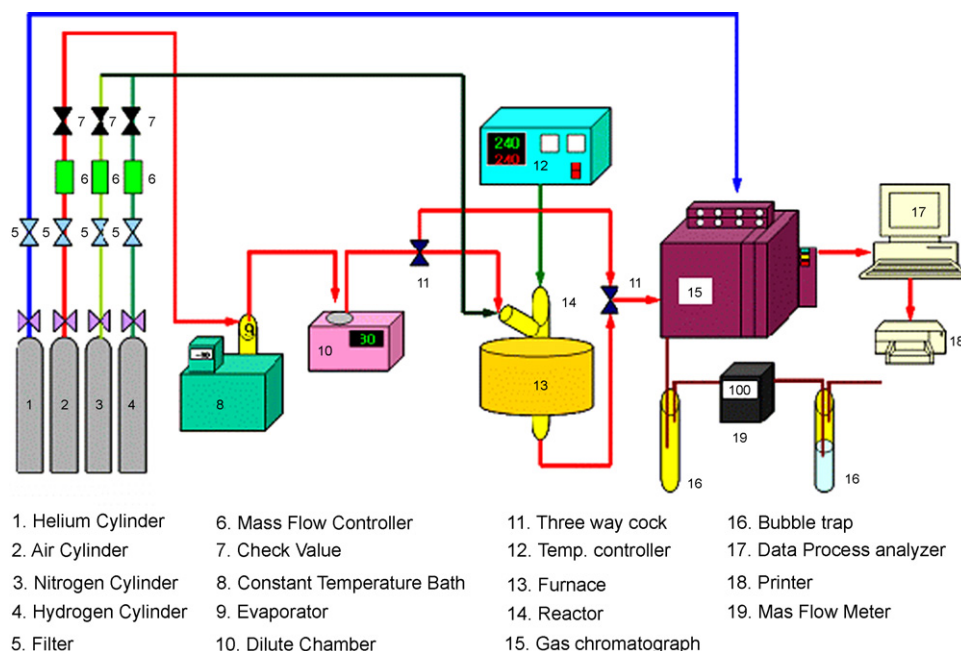
Fig. 1. Schematic of the experimental apparatus.

1. Helium Cylinder	6. Mass Flow Controller	11. Three way cock	16. Bubble trap
2. Air Cylinder	7. Check Value	12. Temp. controller	17. Data Process analyzer
3. Nitrogen Cylinder	8. Constant Temperature Bath	13. Furnace	18. Printer
4. Hydrogen Cylinder	9. Evaporator	14. Reactor	19. Mas Flow Meter
5. Filter	10. Dilute Chamber	15. Gas chromatograph	

was loaded in the middle of the reactor supported by quartz wool. Benzene, toluene and o-xylene (BTX) were purchased from Fisher and used without further treatment. An air stream bubbling through a saturator filled with liquid hydrocarbon carried an individual vapor. For accurate and stable controlling the gas flow rates, mass flow controllers (UNIT Instrument, UFC-8100) were employed. The concentrations of BTX were 1000 ppm, controlled by the temperature of the saturator and mixed with another air stream. The flow rate of gas mixture through the reactor was 100 ml min^{-1}. All lines were heated sufficiently at 120 °C to prevent the adsorption and condensation of reactants and products in the tubes. The catalytic activities of selected samples were examined in the temperature range of 200–500 °C with an interval of 20 or 30 °C. Experimental data were collected after ensuring the steady state condition in each step.

The concentration of inlet and exit gas stream was determined using a gas chromatograph, GC-14A model (Shimadzu) equipped with thermal conductivity. The chromatographic column used was composed of a 5% bentone-34 and 5% dinonyl phthalate/shimalite (60–80 mesh, 3 mm Ø × 3 m) for BTX analysis, and a Porapak Q (50–80 mesh, 3 mm Ø × 3 m) was used for CO_2 separation. The GC/MS (Shimadzu, QP5050) was also employed for the quantitative and qualitative analysis of the products and by-products. In the present work, the only products were CO_2 and H_2O and other by-products were not found under most experimental conditions. The conversion was calculated based on the hydrocarbon consumption.

3. Results and discussion

A blank test was conducted without a catalyst to examine the effect of the quartz wool and the quartz reactor. No homogeneous reaction was observed below 600 °C.

3.1. Effect of air pretreatment

The BET surface areas of the copper based spent catalysts pretreated with air and hydrogen at three different temperatures (200, 300, and 400 °C) are presented in Table 2, and the amounts of coke deposition on the spent catalyst and the air pretreated spent catalyst are listed in Table 3. Sulfur known as a catalyst poison material was not detected in the spent catalyst. The BET surface areas for the air pretreated spent catalysts are similar (156–159 m^2 g^{-1}), within the experimental error, and they practically do not change with the pretreatment temperature; however, the amount of coke deposition on the surface of the spent catalyst decreases (2.74 → 0.54 wt%) with increasing the pretreatment temperature, indicating that the removal of carbon has an insignificant effect on the BET surface area. The XRD patterns of all the air pretreated spent catalysts (Fig. 2 (top)) show diffraction peaks for the CuO and γ-Al$_2$O$_3$, and the XRD patterns against with the increment of pretreatment temperatures show no significant change. As shown in Fig. 2 (bottom), their TPR profiles reveal one main peak with a shoulder which is similar to that of the spent catalyst. This result indicates that the air pretreatment may have an insignificant effect on regenerating the copper based spent catalyst.

Table 2

BET surface area of the copper based spent catalyst pretreated with air and hydrogen at different temperatures

Pretreatment temperature (°C)	BET surface area (m^2 g^{-1})	
	Air	Hydrogen
200	156	156
300	157	156
400	159	157

Table 3
Coke deposition of the copper based spent catalyst pretreated with air at different temperatures

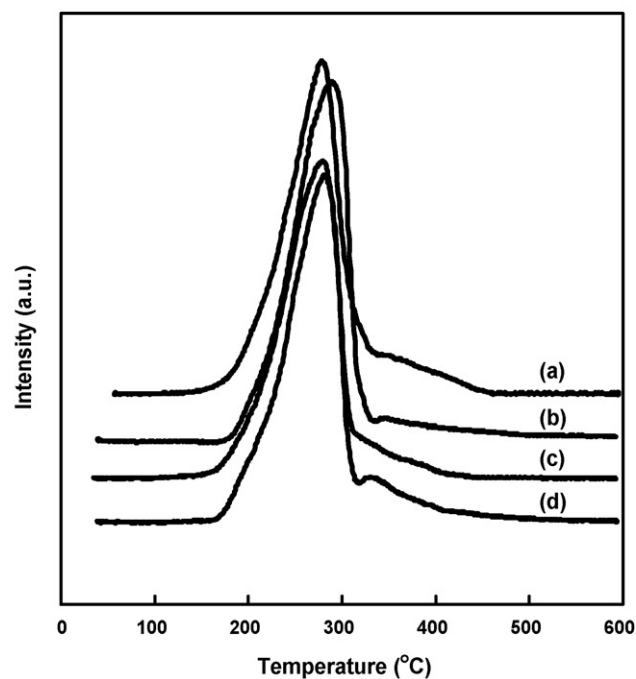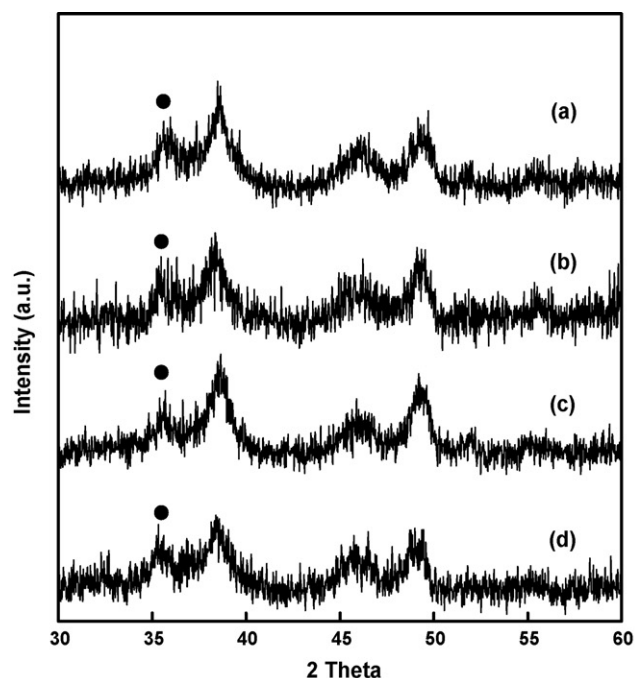| Pretreatment temperature (°C)	The amount of coke deposition (wt%)
None[a,b]	2.74
200	1.46
300	1.40
400	0.54

[a] None denotes no pretreatment.
[b] No sulfur detected.

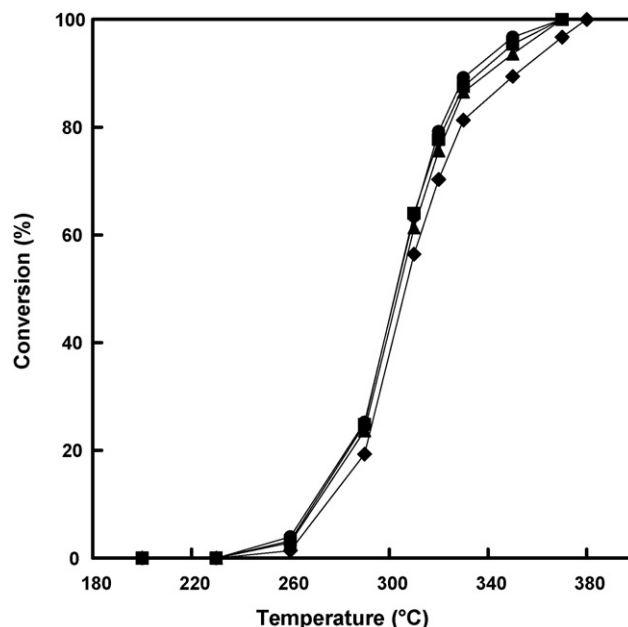Fig. 2. XRD pattern (top) and TPR profile (bottom) of the copper based spent catalyst pretreated with air. (●) CuO; (a) none, (b) 200 °C, (c) 300 °C, and (d) 400 °C.

Fig. 3. Toluene conversion over the copper based spent catalyst pretreated with air. Reaction condition: catalyst weight = 1.0 g, toluene concentration = 1000 ppm in air, total flow rate = 100 ml min^{-1}. (●) none, (■) 200 °C, (▲) 300 °C, and (◆) 400 °C.

Fig. 3 shows the toluene conversion as a function of reaction temperature over the pretreated spent catalysts. The conversion profiles shift slightly to higher temperatures with an increasing pretreatment temperature. On the whole, the oxidized samples are less active than the spent catalyst. Even though the air pretreatment decreases the coke deposition, its catalytic activity is not an appreciable one. These results indicate that air pretreatment is not effective in regenerating the copper based spent catalyst. In addition, this result is also quite similar to that of our previous study of complete oxidations of VOCs over the pretreated palladium based spent catalyst [19].

3.2. Effect of hydrogen pretreatment

As shown in Table 2, the BET surface areas of the copper based spent catalyst pretreated with hydrogen at three different temperatures (200, 300, and 400 °C) are almost constant, which suggests that the temperatures of hydrogen pretreatment also have an insignificant effect on the BET surface area. Their XRD patterns are shown in Fig. 4 (top). The CuO phase is present mainly in the spent catalyst. A new Cu^0 diffraction peak appears in the hydrogen pretreated spent catalysts, and it increases from 200 to 400 °C with increasing the pretreatment temperature, whereas the CuO diffraction peak disappears. Accordingly, the reduction by hydrogen results in changing the CuO phase into the Cu^0 phase. The TPR profiles of the spent catalyst and the pretreated spent catalysts are shown in Fig. 4 (bottom). The reduction profile changes significantly as the temperature of hydrogen pretreatment increases. Increasing the temperature of hydrogen pretreatment results in shifting the reduction peak to lower temperature and decreasing the peak intensity greatly.
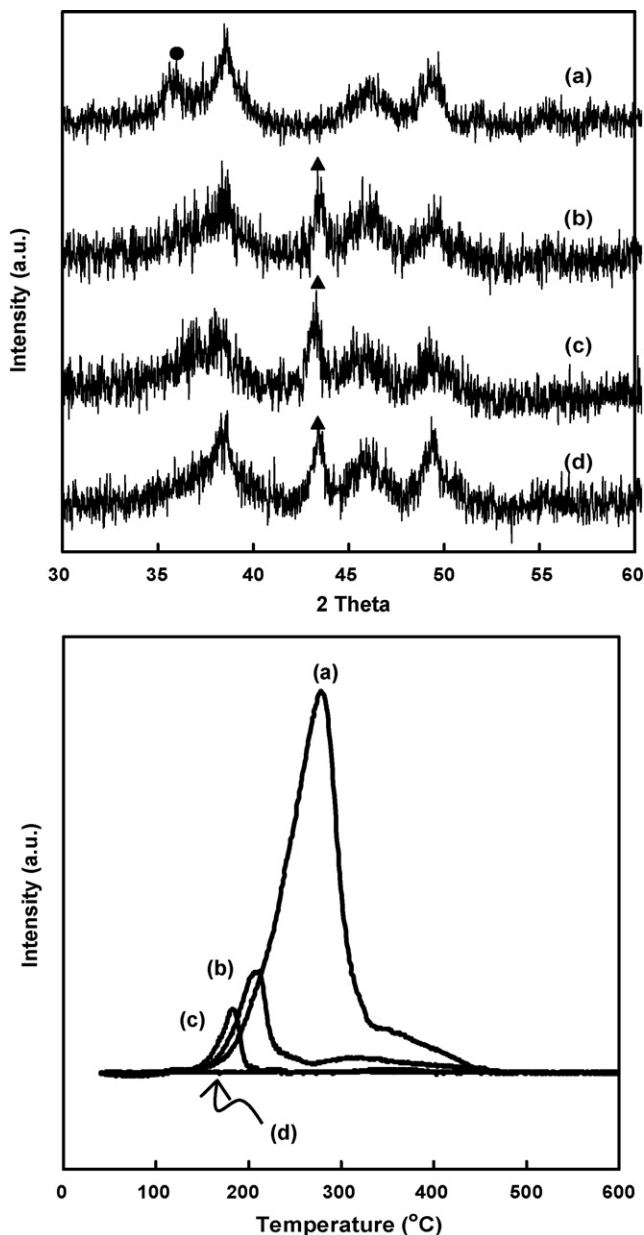
Fig. 4. XRD pattern (top) and TPR profile (bottom) of the copper based spent catalyst pretreated with hydrogen. (▲) Cu, (●) CuO; (a) none, (b) 200 °C, (c) 300 °C, and (d) 400 °C.

A great decrease in peak intensity according to the increase of pretreatment temperatures explains well why the Cu^0 phase was mainly present in (b), (c) and (d) of Fig. 4 (top). The TPR profile of the spent catalyst shows one main peak at 282 °C with a shoulder at 360 °C. A main peak located at 214 °C with a shoulder at 320 °C is observed in that of the spent catalyst pretreated at 200 °C. Only one peak at 186 °C with a trace shoulder is observed in that of the spent catalyst pretreated at 300 °C. The reduction peak disappears in that of the spent catalyst pretreated at 400 °C. Even though the XRD data indicate as shown in Fig. 4 (top) that the Cu^0 phase alone is predominantly present in the spent catalyst pretreated with hydrogen at 200 and 300 °C, we cannot rule out the existence of CuO and Cu_2O species. The double peak must have been

assigned to the reduction of CuO. The double structure is probably caused by a two-step ($Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$) reduction occurring slightly at different temperatures [20–22]. The peaks at the range between 186 and 282 °C are attributed to the reduction of CuO to metal Cu^0, and those at the range from 320 to 360 °C are attributed to the reduction of Cu_2O to metal Cu^0. Therefore, these results may indicate that CuO is prevalently reduced to metal Cu^0 and partially to Cu_2O. This Cu_2O is reduced again into metal Cu^0 in this experimental condition.

XPS was conducted to obtain the information on the elemental compositions and the oxidation state. Fig. 5 shows the XPS spectra (Cu 2p). The well-defined shake-up satellites observed in the spent catalyst at 954.5 and 943.8 eV on the high binding energy side of the copper core line $2p_{3/2}$ (centered at 934.5 eV) are typical of Cu^{2+} species attributed to multiple splitting. The existence of strong satellite features for Cu 2p indicates that there is no possibility of the presence of Cu_2O phase [23]. All this information is consistent with the XRD result which indicates that copper species in the copper based spent catalyst is mainly in the form of CuO. In the case of the copper based spent catalyst pretreated with air at 200 °C, the binding energy of Cu $2p_{3/2}$ is found to be 934.9 eV. This result means that copper species of this catalyst are also present mainly in the form of CuO in a way similar to the spent catalyst. However, in the case of the copper based spent catalyst pretreated with hydrogen (at 200, 300 and 400 °C), the shake-up satellites (at 954.5 and 943.8 eV) almost disappear, and the binding energies of Cu $2p_{3/2}$ shift to lower binding energies, which are 934.1, 932.7 and 932.9 eV, respectively. It has been reported that the binding energies of $Cu^+(Cu_2O)$ and Cu^0 are 932.6 and 932.8 eV, respectively [24]. Thus, it seems that $Cu^+(Cu_2O)$ species as well as Cu^0 is present in the copper based spent catalyst pretreated with hydrogen at 200 and 300 °C, and
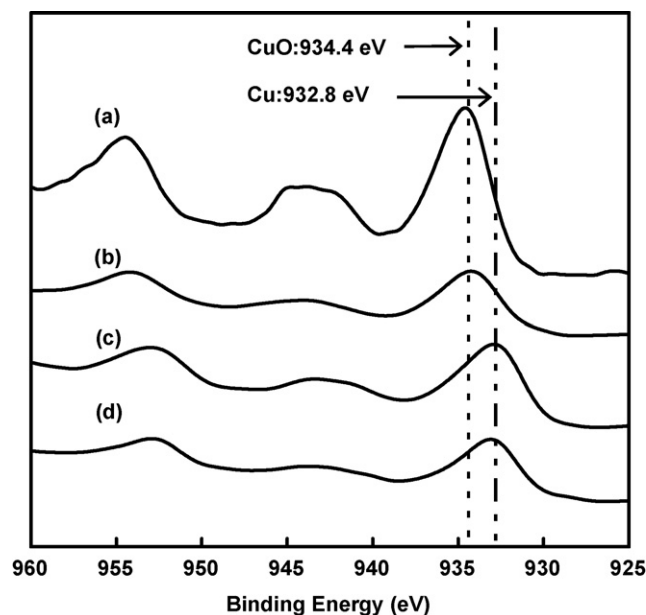

Fig. 5. XPS spectra of the copper based spent catalyst pretreated with hydrogen. (a) none, (b) 200 °C, (c) 300 °C, and (d) 400 °C.
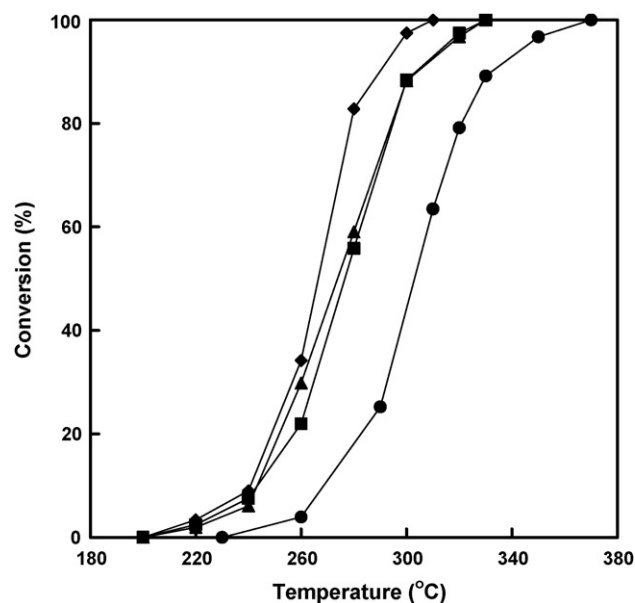
Fig. 6. Toluene conversion over the copper based spent catalyst pretreated with hydrogen. Reaction condition: catalyst weight = 1.0 g, toluene concentration = 1000 ppm in air, total flow rate = 100 ml min^{-1}. (●) none, (■) 200 °C, (▲) 300 °C, and (◆) 400 °C.

Cu^0 is present in the copper based spent catalyst pretreated with hydrogen at 400 °C.

Fig. 6 shows toluene conversion with respect to the reaction temperature over the copper based spent catalyst pretreated with hydrogen at different temperatures. The conversion profiles considerably shift to lower temperatures with increasing pretreatment temperature. The spent catalyst and the spent catalysts pretreated with hydrogen at 200, 300, and 400 °C achieve the complete oxidation of toluene at the reaction temperatures of 360, 330, 330, and 310 °C, respectively, and the temperatures for 50% toluene conversion are 303, 273, 271 and 267 °C, respectively. Thus, the activity sequence of the copper based spent catalyst with respect to the temperature of hydrogen pretreatment is 400 °C > 300 °C ≥ 200 °C > none. Consequently, it appears that the catalytic activity of the spent catalyst is associated with lower copper oxidation state, and the catalytic activity increases with decreasing copper oxidation state. These findings strongly support that the hydrogen pretreatment endowing the metallic form have a significantly beneficial effect on the catalytic combustion of toluene, and that the pretreatment temperature is a crucial factor in regenerating the spent catalyst.

Table 4
BET surface area and copper concentration of the copper based spent catalyst pretreated with 0.1N of different acid aqueous solutions

Acid	BET surface area (m^2 g^{-1})	Cu concentration (wt%)
HNO$_3$	159	7.6
HCl	164	7.2
CH$_3$COOH	156	7.3
H$_3$PO$_4$	176	6.1
H$_2$SO$_4$	175	4.4

3.3. Effect of different acid pretreatments

Table 4 shows the BET surface areas and copper concentrations of the spent catalysts pretreated with different acid aqueous solutions. The order of the BET surface areas and that of copper concentrations of the pretreated spent catalysts according to each acid aqueous solution are found to be $H_3PO_4 > H_2SO_4 > HCl > HNO_3 > CH_3COOH >$ none, and none $> HNO_3 > CH_3COOH > HCl > H_3PO_4 > H_2SO_4$, respectively. This means that the acid pretreatment brought about an increase in the BET surface area, while it decreases the copper concentration owing to the removal of impurities or copper from surface and pores of the spent catalysts.
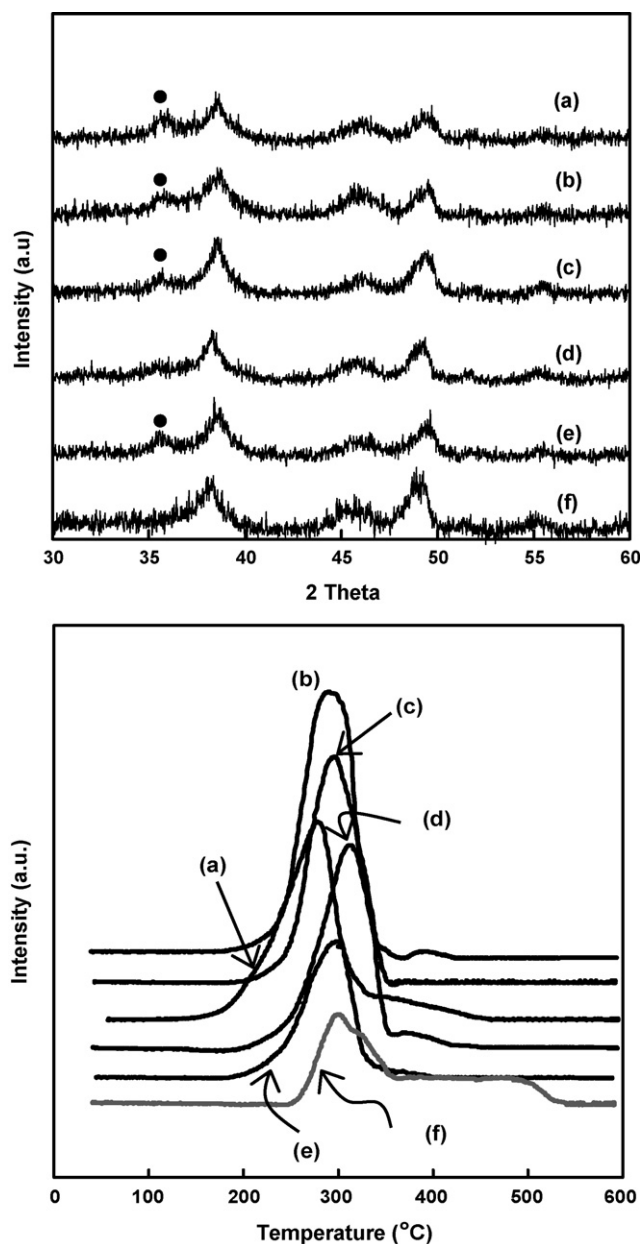

Fig. 7. XRD pattern (top) and TPR profile (bottom) of the copper based spent catalyst pretreated with different acid aqueous solutions. (●) CuO; (a) none, (b) HNO$_3$, (c) HCl, (d) H$_3$PO$_4$, (e) CH$_3$COOH, and (f) H$_2$SO$_4$.

The XRD patterns of these catalysts are shown in Fig. 7 (top). The CuO diffraction peaks are observed in the spent catalyst pretreated with nitric acid, acetic acid, and hydrochloric acid solutions, but they disappear in the spent catalyst pretreated with phosphoric acid and sulfuric acid solutions. Their TPR profiles are shown in Fig. 7 (bottom). The main reduction peak of the copper based spent catalyst pretreated with acid aqueous solutions starts to emerge at temperatures 30–100 °C higher than that of the spent catalyst. In addition, the reduction in the area of the copper based spent catalyst pretreated with two acid aqueous solutions (phosphoric acid and sulfuric acid) is observed in the TPR profile. The intensity of the TPR peak according to each acid aqueous solution is also observed in the order of $HNO_3 > CH_3COOH >$ none $> HCl > H_3PO_4 > H_2SO_4$.

Fig. 8 shows the toluene conversion as a function of reaction temperature over these catalysts. The catalytic activities of the acid treated samples are found in the following order: $HNO_3 > CH_3COOH >$ none $> HCl > H_3PO_4 > H_2SO_4$. The spent catalysts pretreated with nitric, acetic, hydrochloric, phosphoric and sulfuric acid solutions achieve the complete oxidation of toluene at reaction temperatures of 350, 355, 380, 420 and 470 °C, respectively. The differences in temperature values for the complete oxidation between the spent catalyst (360 °C) and nitric, acetic, hydrochloric, phosphoric and sulfuric acid treated spent catalysts are -10, -5, 20, 60 and 110 °C, respectively. These results indicate that catalytic activity is not related to the BET surface area, while it is related to copper concentration and the intensity of the TPR peak except the spent catalyst. In addition, the slight increment in the intensity of the TPR peak of the spent catalyst pretreated with the nitric acid or acetic acid means an increase in the copper species (active sites) on the catalyst surface. Accordingly, the

nitric acid and acetic acid pretreatments have a little positive effect on the catalytic activity owing to the effectively regenerated active sites on the spent catalyst.

3.4. Stability of the pretreated catalyst and their activity for other reactants

Based on the hydrogen pretreatment selected as the most favorable pretreatment condition in the primary analysis, its stability was investigated with respect to the reaction temperature of 310 °C. As shown in Fig. 9 (top), 100% toluene conversion is maintained for 48 h at the reaction temperature of 310 °C. This means that the stability of spent catalyst is meaningfully good. In addition to toluene, we carried out the oxidation of benzene and *o*-xylene to investigate the catalytic activity in the VOC molecules. As shown in Fig. 9

Fig. 9. Stability test of toluene conversion (top) over the copper based spent catalyst pretreated with hydrogen (400 °C) and BTX conversion (bottom) over the same catalyst. Reaction condition: catalyst weight = 1.0 g, benzene, toluene or *o*-xylene concentration = 1000 ppm in air, total flow rate = 100 ml min^{-1}. (●) Benzene, (■) toluene, and (▲) *o*-xylene.
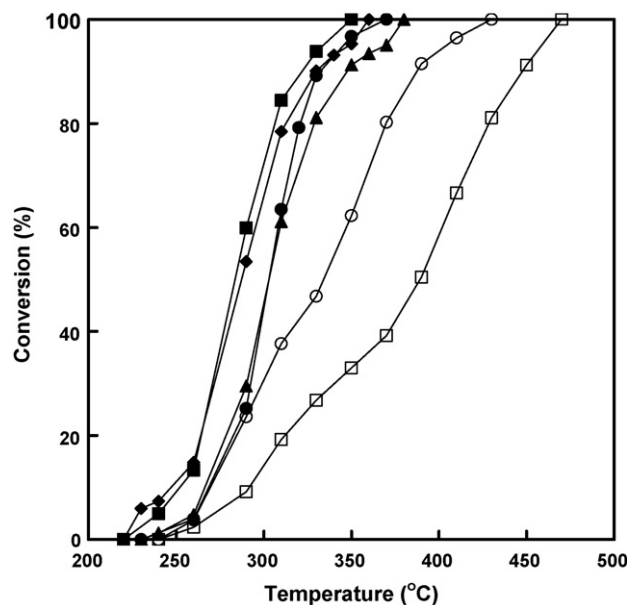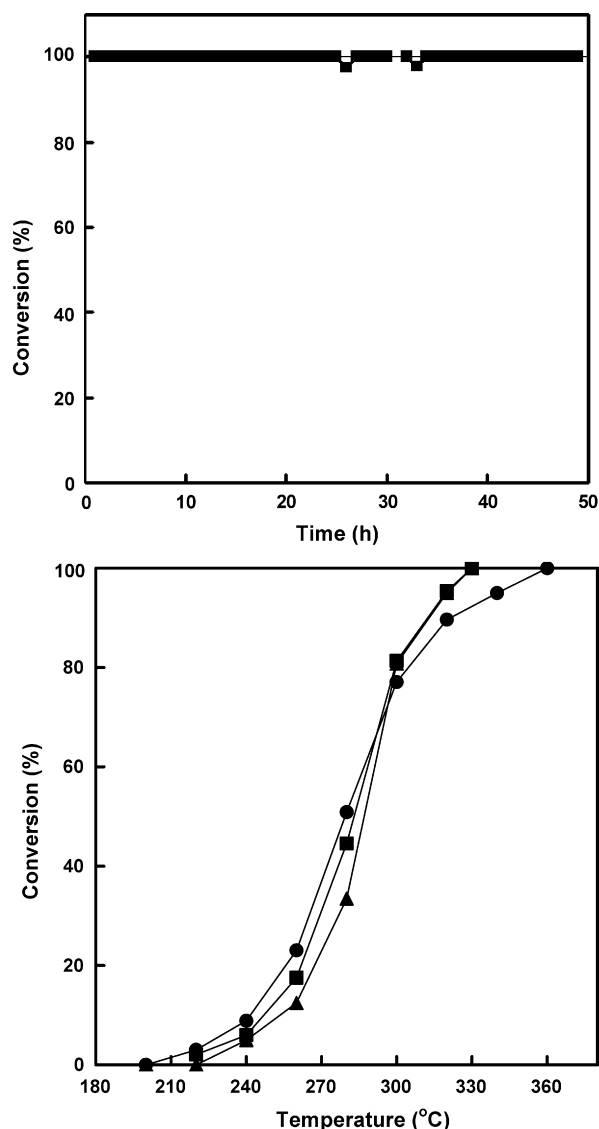

Fig. 8. Toluene conversion over the copper based spent catalyst pretreated with different acid aqueous solutions. Reaction condition: catalyst weight = 1.0 g, toluene concentration = 1000 ppm in air, total flow rate = 100 ml min^{-1}. (●) none, (■) HNO_3, (▲) HCl, (◆) CH_3COOH, (○) H_3PO_4, and (□) H_2SO_4.

(bottom), the order of BTX oxidation activity over the copper based spent catalyst pretreated with hydrogen at 400 °C is found to be: benzene > toluene > *o*-xylene at a low oxidation temperature, and toluene $\geq$ *o*-xylene > benzene at a high oxidation temperature. These results indicate that there may be two different mechanisms for the oxidation of BTX over this catalyst: the aromatics associated with the methyl groups and the aromatics without the methyl groups. The former is more difficult to oxidize than benzene [25] at a low oxidation temperature and is easier to oxidize than benzene [26] at a high oxidation temperature.

4. Conclusions

The catalytic combustion of BTX over the copper based spent catalyst modified by different pretreatment techniques was carried out to assess the possibility of recycling the spent catalyst. The results obtained from the catalytic combustion of toluene revealed that the copper based spent catalyst had a good catalytic activity, even though the activity and selectivity of the regenerated catalyst were not sufficient enough to reapply to the original process. Moreover, the catalytic activities of the pretreated spent catalyst were highly dependent on the treatment methods. Air pretreatment had no positive effect on the catalytic activity of the spent catalyst, although it decreased the amount of the coke deposition on the spent catalyst. With increasing the temperature of hydrogen pretreatment, the catalytic activity considerably increased, and the reduction of copper oxidation state (CuO $\rightarrow$ Cu$_2$O $\rightarrow$ Cu) was observed. The nitric acid and acetic acid pretreatment had a little positive effect on the catalytic activity owing to the effectively regenerated active sites (copper species) on the spent catalyst. The hydrochloric acid, phosphoric acid or sulfuric acid pretreatment had a negative effect on catalytic activity because of the active site reduction on the copper based spent catalyst. The hydrogen pretreatment endowing the metallic copper was much superior to air or acid pretreatments for regenerating the spent catalyst because Cu^0 was the most active to remove toluene. Moreover, the spent catalyst pretreated with hydrogen showed a favorably stable catalytic activity in a long-term test. The catalytic activity sequence with respect to VOCs molecules indicated that there might be two different reaction mechanisms for the catalytic combustion of BTX over the copper based spent catalyst pretreated with hydrogen: the aromatics associated with the methyl groups were difficult to oxidize at a low reaction temperature; the aromatics without the methyl groups were difficult to oxidize at a high reaction temperature. Consequently, the copper based spent catalyst pretreated with hydrogen could be recommended as the catalyst for the catalytic combustion of VOCs.

Acknowledgement

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